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VOL. 14, SEC. A. SEPTEMBER, 1936 NUMBER 9

A LARGE QUARTZ SPECTROGRAPH FOR EXAMINATION OF BIOLOGICAL MATERIAL[1]

BY J. S. FOSTER[2]

Abstract

A quartz spectrograph with Cornu prism is described, in which are combined low cost, unusually high dispersion, and convenience of operation. The general construction is outlined and special fittings are treated in detail.

Introduction

A quartz spectrograph is preferable for the general quantitative spectrographic examination of biological material, since the most sensitive spectral lines of many elements lie in the ultra-violet region. Grating spectrographs are, for the present purpose, too erratic as regards their intensity characteristics. Owing to the multitude of elements commonly represented in a biological sample, a high dispersion is not infrequently required to separate the spectral lines of special interest. Moreover, the scattered light in the camera must be reduced sufficiently to permit the low smooth background needed for the sensitive detection of elements, and for the quantitative measurement of line intensities. Since in most studies a very large number of analyses must be carried out, convenience of operation is a further property of the instrument which is greatly to be desired.

The cost of a really good and efficient instrument for research of this kind may be considered prohibitive by many investigators. A good solution lies in the spectrograph to be described. It has been found possible to build at a surprisingly low cost an instrument that meets all requirements and rises to a high standard of efficiency and convenience of operation.

Description of the Instrument

When employed for investigations in the ultra-violet regions, the instrument consists of the following essential quartz parts arranged in the usual manner:

(1) Collimator lens; diameter, 88 mm.; focal length, 150 cm.

(2) Camera lens; diameter, 88 mm.; focal length, 250 cm.

(3) 60° prism with faces 100 mm. × 56 mm.

[1] *Manuscript received July 17, 1936.*
Contribution from the Department of Physics, McGill University, Montreal, Canada.
[2] *Macdonald Professor of Physics, McGill University.*

For improved dispersion in the visible region, the above-described prism is replaced by

(1) A glass prism of the same size, and

(2) A 30° prism of very dense glass.

The instrument therefore does double duty, providing, as it does, excellent dispersion in both visible and ultra-violet regions of the spectrum.

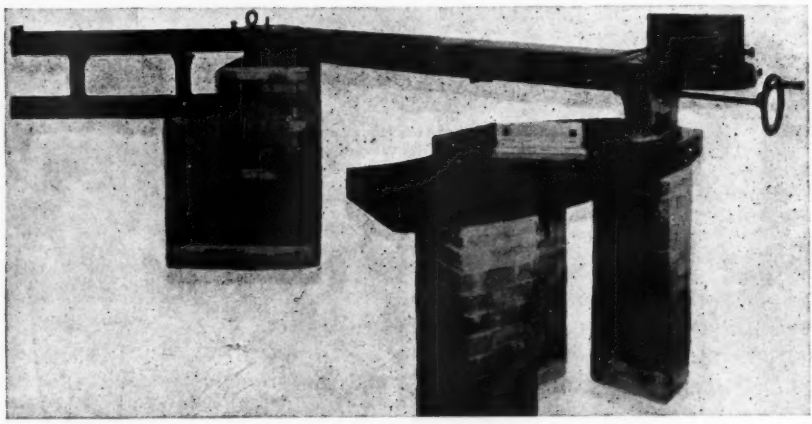

FIG. 1.

As may be learned from Fig. 1, the spectrograph rests on a brick, cement, and slate foundation. The chief elements entering into its construction are described briefly in the following paragraphs.

(1) *The Slit*

The slit of stainless steel was made by Mr. H. T. Pye and was built into the face of the collimator tube. Since independent means for focusing the collimator is provided, this construction has an advantage in that the slit cannot be twisted from its vertical position. The effective length of the slit is one inch. It may be conveniently opened to an unusual width when a "step slit" intensity marker is being used.

(2) *The Holder for Slit Masks*

This is a time saving device. It includes small permanent magnets which hold the sheet iron masks. The holder may slide between adjustable stops and thus permit rapid adjustments for comparison spectra, etc. It may, at any time, be turned back out of the way without the loss of adjustment.

(3) *The Collimator Tube*

This tube telescopes to positions which insure that the beam of light which reaches the centre of the plate will be parallel in its course through the prism. In its construction, two long channel irons were beveled,—one externally and

the other internally—so that the irons may be fitted one inside the other and may slide on the accurately planed surfaces. Each channel iron serves as the base of a tube of rectangular cross section which is formed from sheet furniture steel. The exact adjustments of the collimator corresponding to each spectral region is made reproducible by a series of steel blocks, or stops, attached underneath the inner channel iron. These make contact with a spring catch on the outer iron.

(4) *The Circular Prism Chamber*

This is of heavy cast iron, with double walls. The inner portion supports—directly or indirectly—the prism and the two lenses, while the closely fitting outer section supports the front end of the camera box. Although the cylindrical surfaces are opened up to let the light in and out, there is enough overlap to keep the chamber light-tight when the camera is rotated to all necessary positions.

The inner wall of the chamber is set with bolts into a heavy brick and cement pillar. It carries directly the collimator lens. A steel floor supports the mounts for the prism and camera lens. The latter mount is pivoted at the centre of the chamber and is rotated as necessary through a pivoted connection with the outer wall of the chamber. The prism mount revolves about an axis so chosen, with respect to the centre of the chamber, that the light beams automatically are kept symmetrical with respect to the camera lens in all positions. The angular position of the prism is changed by a screw which is operated from the outside. The exact positions may be reproduced by means of the optical lever partly shown in Fig. 1.

For work in the visible region, the above-mentioned prism mount is moved about an inch and a half toward the collimator, and the 30° prism together with its platform is dropped into position on the mount of the camera lens.

(5) *The Camera*

The framework at the front of the camera box is so designed as to place the contacts with the outer wall of the prism chamber (pivots) in such positions that there is no interference with the collimator tube when the camera is moved to any of its standard positions. In the rear of this special casting, the sides of the telescoping camera box consist of channel irons arranged on edge but otherwise fitted exactly as in the collimator tube. Through the spacing and rigidity provided by the front and rear castings together with simple supplementary features, the camera box has an entirely satisfactory rigidity. It is easily adjusted for focus by a heavy screw which lies under the box, and is operated from the rear of the instrument as indicated in the photograph.

The mounting for the plate holder has some features in common with the largest Hilger spectrographs. One vertical cylindrical casting fitted inside another permits the plate to be rotated about a vertical axis through the centre of the emulsion. The holder is completely enclosed in a light-tight compartment. The slide is drawn from the side while the holder is at the top of

the enclosure, and the plate is then racked down into position for an exposure. The tilt of the plate is recorded on a suitable scale.

A pointed steel rod held by a spring in a vertical V-block is mounted on the base of the rear casting of the camera. It may be depressed to make, on the table, a mark that records exactly the position of the camera.

Method of Focusing the Spectrograph

At the rear of the collimator tube is a Hartmann diaphragm. This is built into a circular frame, and swings on a vertical hinge at one end of the horizontal diameter. By means of a shaft which projects through the top of the collimator tube, the diaphragm may be turned into the beam or swung back against the wall of the tube. When in position, the collimator lens is flooded on only one side of a vertical diameter. The diaphragm may be rotated through 180° (by pulling the cords attached to the ends of the small spheres shown near the prism chamber in the photograph), so that only the other half is flooded.

The instrument is focused in the following manner. Spectra of the iron arc are taken for comparison with the diaphragm in its two positions. If the spectral lines match at all wave-lengths, the spectrograph is in focus. If they "stagger" at any point, one can tell from the sense and magnitude of the displacement the direction and approximate extent of the motion of the plate to bring it into focus.

By this method one not only saves a great deal of time, but may be assured in the end that the instrument is really in focus. The writer is indebted to Dr. J. S. Plaskett for the suggestion that the Hartmann method be used to secure good focus.

Each selected adjustment of the spectrograph is permanent in the sense that it can be reproduced accurately, and hence the instrument need be focused but once for each region. Thus one may immediately obtain a plate in good focus in any region of the spectrum, or can by successive exposures on one plate examine as much of the spectrum as is desired.

In the extreme ultra-violet, dispersion becomes better than one Ångstrom per millimetre.

Acknowledgments

Financial assistance from the Rockefeller Foundation is gratefully acknowledged.

The mountings in this instrument have been made with great skill by Mr. H. T. Pye in the shop of the Macdonald Physics Laboratory.

A GAS-TIGHT FURNACE FOR THERMOCOUPLE STANDARDIZATION[1]

By C. D. Niven[2]

Foote, Fairchild and Harrison (1) have described in detail, a furnace for calibrating a platinum-platinum-rhodium primary standard thermocouple in molten metals. In following out the description given by them, the writer encountered two difficulties which did not seem to be adequately dealt with. One of these was the removal of the crucibles from the furnace without turning the furnace upside down, and the other was the provision of a gas-tight space above the crucible for melting down metal for the first time. In the case of copper a reducing atmosphere other than that afforded by graphite powder is very desirable whenever the metal is being melted. This is necessitated by the fact that the oxide of copper is soluble in the molten metal. The slight oxidation which occurs at the lower temperatures when the graphite is not very active as a reducing agent is not entirely prevented, and when the copper is removed from the crucible after a melting point determination it will be found oxidized if graphite alone is used as the reducing agent. When the copper is melted down again no doubt much of the oxide is reduced, but on the whole this alternate oxidation and reduction cannot be considered desirable, especially when the melting point of copper is affected by the amount of dissolved oxide it contains.

In order to maintain a reducing atmosphere over the surface of the crucible, a cap made to fit over the top of the furnace was at first used, and the joint was made gas-tight with wax. This waxed joint was fairly satisfactory with a metal of low melting point; but in the case of copper the use of wax was most unsatisfactory owing to the high temperature employed, and gas was continually entering the room. The gas leaked past the insulators separating the electrical leads from the metal case, and also between the asbestos board forming the bottom of the furnace and the metal case. The objectionable odor of the gas in the room might have been overcome by putting the whole apparatus in a fume cupboard, but this would have rendered the apparatus inconvenient.

The other plan was therefore adopted, namely, to redesign the furnace so that it was definitely gas-tight. In the original furnace, which had been designed according to the specifications of Foote, Fairchild and Harrison, the diameter of the metal cylinder which contained the diatomite powder surrounding the heating coil and alundum tube was 7 in. In the new design the cylinder was 12 in. in diameter. This increase in size prevented the possibility of solder melting, and permitted the soldering of discs of sheet brass to the bottom and top. It also permitted the soldering of two tubes to

[1] *Manuscript received September 1, 1936.*
Contribution from the Division of Physics, National Research Council, Ottawa, Canada.
[2] *Physicist, National Research Laboratories, Ottawa.*

the side of the cylinder through which the lead wires could be carried. The object of these tubes was to allow the leads to be waxed in, by stopping the conduction of too much heat from the cylinder to the wax. The escape of gas can, in this manner, be completely prevented—except at the lid—provided that the soldering is done carefully. It was not possible to do away with a low temperature jointing material, such as wax, for the lid, and so this necessitated the use of a water cooled lid.

Fig. 1 shows in detail, the lid of the furnace as finally constructed. The lid, *A*, consisted of a piece of solid brass plate 3 in. square by 0.5 in. thick. By

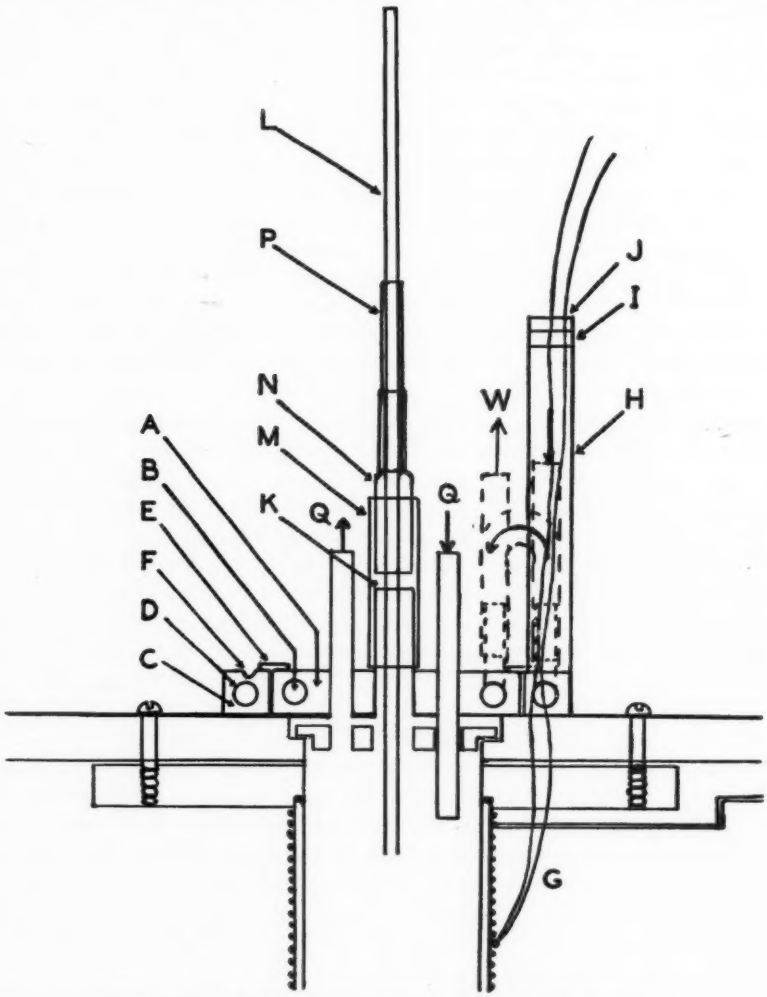

FIG. 1 *Diagram of the water-cooled gas-tight lid of the furnace.*

boring the holes *B*, parallel to the edges of this plate, and by plugging their ends it was possible to get a path *W* for the circulation of water in the lid, sufficiently large to keep it cool. It was hoped that the thermal contact with the top of the furnace casing would prevent the wax from melting when the plate was placed on the furnace, but experience proved that this was not so.

It was therefore necessary to water-cool the top of the furnace. A 4 in. square piece of half-inch brass plate *C* was taken, and a 3 in. square was cut out of its centre so that the lid could easily fit into it, and a channel *D* for the circulation of water was made by boring and plugging as in the case of the lid itself. In order to prevent the wax from going down into the crack when the lid was waxed on, a thin flange *E* was soldered to the lid in such a way that it overlapped the 4 in. square of brass; in the latter a slight groove *F* was made to help to hold the wax.

Foote, Fairchild and Harrison recommend the use of a thermocouple on the nichrome winding itself. The wires from this couple *G* were brought out through a tube *H* brazed into the top of the casing. This tube came in contact with the 4 in. brass square carrying the cooling water and was thus kept cool. The electrical insulation *I* through which the thermocouple wires passed could then be made gas-tight with wax *J*.

Through the centre of the 3 in. brass square used for the lid a hole was bored to permit the introduction into the furnace of the quartz sheath *L* of the standard thermocouple. A brass tube *K* was soldered to the lid concentric with this hole, and a short piece of rubber tubing *M* connected the brass tube with a short brass reducing piece *N* carrying a small piece of rubber tubing *P* chosen to fit the quartz sheath snugly without gripping it unnecessarily. It was important to choose this piece of tubing correctly, as otherwise it would have been impossible to slip the sheath up and down into the furnace without unnecessary friction.

Owing to the fact that the insulation casing on this furnace was large, it was desirable to have some convenient means to take out the crucible. A photograph of a device found to answer this purpose is shown in Fig. 2. It consisted of a wooden tube split half way up in two directions parallel to its axis so that the wall could be forced to expand and grip the crucible on the inside. The wall was forced to expand by drawing up a cone into the tube by means of a screw. This cone is shown in the photograph projecting at the bottom of the wooden tube. It was necessary to exercise a little care in screwing back the cone because sufficient force can easily be exerted to crack the cylindrical wall of the porcelain crucible.

FIG. 2

In circulating the gas from a gas jet or from a cylinder containing nitrogen through the copper tubes *Q*, it is

unwise to let too rapid a stream of gas pass, as this has a marked cooling effect on the furnace. In actual practice the writer filled the furnace up with graphite, and as a rapid stream had the effect of blowing out the powder this was another reason for maintaining as small a flow of gas as possible.

Owing to the fact already stated that it is at low temperatures that the atmosphere of coal gas or nitrogen is most important, since the graphite is then non-reactive, the gas should not be turned off until the furnace is cold. If this precaution be taken, then, when the solidified copper is taken out of the crucible, it will be found bright instead of covered with a coating of dark oxide.

Acknowledgment

In conclusion the writer wishes to express his indebtedness to Mr. A. C. Halferdahl for many helpful suggestions.

Reference

1. FOOTE, P. D., FAIRCHILD, C. O., and HARRISON, T. R. Tech. Papers Bur. Standards, 170 : 195-196. 1921.

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CHEESE-RIPENING STUDIES

THE INFLUENCE OF YEAST EXTRACT ON THE TYPES OF STREPTOCOCCI FOUND IN STARTERS[1]

BY BLYTHE ALFRED EAGLES[2], OLGA OKULITCH[3] AND ALEXANDER GRAHAM CAMPBELL[4]

Abstract

The influence of yeast extract on the bacterial flora of commercial cheese starters has been studied.

The addition of yeast extract to the starter milk appears to favor the development of a larger proportion of slow acid-producing strains of streptococci with the ability to ferment the more complex carbon sources.

New strains of lactic acid streptococci are described.

The possibility of adding yeast extract as an enrichment to the milk used for the carrying of commercial starters was first suggested by Orla-Jensen (4). In a preliminary study on the use of yeast extract for the carrying of starters for cheese-making, the authors found that a starter carried in the usual manner was much superior to the same starter carried in the yeast-enriched milk. The influence of the yeast extract was to be seen not only in the quality of the starter itself, but also in the vitality of the starter in the cheese vat, and in the quality of the resulting cheese. The results obtained confirm the original findings of Orla-Jensen in regard to the influence of yeast extract on the carrying of starters. In his paper Orla-Jensen (4) states that: "The vitality of the lactic acid bacteria does not seem to be enhanced by the use of yeast extract, but the bacteria would rather seem to become pampered, so that when afterwards cultivated in pure milk they form a little less acid than previous to the cultivation with yeast extract."

In his monograph on the lactic acid bacteria, Orla-Jensen (2) shows that two species of Streptococci—*Sc. cremoris* and *Sc. lactis* constitute the majority of the strong acid-forming organisms to be found in starters, and that starters consisting in large measure of streptococci of the *lactis* type are not as suitable as those starters in which the *cremoris* type predominates. Orla-Jensen and Hansen (3) have shown that closely related species of streptococci are also to be found in starters. While many of the new species reported by Orla-Jensen and Hansen are intermediate between *Sc. cremoris* and *Sc. lactis*,

[1] *Manuscript received August 19, 1936.*
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[4] *Senior Student, Department of Dairying, The University of British Columbia.*

certain of the strains possess the ability of fermenting complex carbon sources which even *Sc. lactis* cannot attack.

In the light of the findings of Orla-Jensen (2) that the best starters seem to have the least power of fermenting the higher sugars, and of the work of Orla-Jensen and Hansen (3) on the variations in sugar-fermenting abilities of the streptococci to be found in starters, it appeared probable that the addition of yeast extract to the starter milk impaired the quality of the starter by encouraging the development and ultimate predominance in the starter of those types of streptococci capable of fermenting the more complex carbon sources. As the work progressed the writers were thus led to enquire into the influence of yeast extract on the bacterial flora of starters.

Experimental

For the study of the influence of yeast extract on the flora of the starter, Hansen's desiccated Lactic Acid Ferment was employed throughout as the source of the organisms used in the building up of the starter. After propagation for 24 hr. in steamed fresh skim milk, the starter was divided into two parts. One portion—Starter *S*—was carried by daily transfers in steamed fresh skim milk; the other portion—Starter *Sye*—was carried in the same fresh steamed skim milk enriched with yeast extract at the rate of 0.15% (5).

After 20 transfers, successive dilutions of the starters were made, and the 1 : 1,000,000 and 1 : 10,000,000 dilutions were plated on Bacto-Peptonized Milk Gelatin of pH 6.76 *(PMG)*, and on the same medium enriched with yeast extract to the extent of 0.15% *(PMGye)*. After incubation at room temperature for seven days, approximately 50 colonies from each starter on *PMG* and on *PMGye* respectively were picked into yeast litmus milk. In order to obtain organisms representative of the flora of each starter on the respective media, all the colonies on a plate were picked. The bacterial count of Starter *S* on both *PMG* and *PMGye* was considerably lower than that obtained for Starter *Sye*. The 42 colonies obtained from Starter *S* on *PMG* were picked from two plates, and the 52 colonies on *PMGye* from three plates. In the case of Starter *Sye*, one entire plate from the *PMG* and *PMGye* plates yielded 47 and 52 colonies respectively.

In the study of the total titratable acidity produced by each strain in milk and in milk enriched with yeast extract, and in the study of the sugar-fermenting abilities of the organisms in casein digest broth, the procedure followed throughout was that employed by Orla-Jensen (1) and by Sadler, Eagles and Pendray (6). The results of the determinations are given in Table I.

Media Employed

Peptonized Milk Gelatin (Difco) of pH 6.76—designated as *PMG*.

Yeast Peptonized Milk Gelatin (Difco) of pH 6.76—peptonized milk gelatin (Difco), enriched with yeast extract at the rate of 0.15% (5) —designated as *PMGye*.

Nutrient Gelatin (Difco).

TABLE I

DISTRIBUTION OF BACTERIAL FLORA IN STARTERS

Strain No.	Per cent Starter		Starter *S*		Starter *Sye*		Lactose	Salicin	Maltose	Starch	Dextrin	Sucrose	Manni-tol	Milk	Yeast milk
	S	*Sye*	*PMG* plate 42 cultures	*PMGye* plate 52 cultures	*PMG* plate 47 cultures	*PMGye* plate 52 cultures									
1	35.1	29.2	16	17	19	10	4.7							5.9	6.5
2	10.6	8.1	7	3	3	5	5.0	4.5						6.5	6.5
3	17.0	17.1	6	10	9	8	5.0	3.4						6.3	7.0
4	6.4	3.0	4	2	2	1	4.5	2.3						5.6	6.5
5	3.3	1.0	1	2	0	1	4.5	3.8	1.6					6.8	7.0
6	0.0	2.0	0	0	0	2	4.3	4.1	3.4					6.1	6.5
7	0.0	1.0	0	0	1	0	5.4	4.1			0.7			6.5	7.0
8	0.0	2.0	0	0	0	2	5.2	3.4				0.7		6.5	6.8
9	1.1	0.0	1	0	0	0	4.5	1.8				2.0		5.6	6.8
10	0.0	1.0	0	0	1	0	4.7	3.8					1.1	7.4	7.7
11	1.1	0.0	0	1	0	0	4.5	2.9					3.2	6.1	6.5
12	2.2	0.0	0	2	0	0	5.2	0.9	0.7	0.5				6.3	7.0
13	4.4	24.1	1	3	11	12	4.5	5.0	3.4	2.7				6.8	6.5
14	1.1	0.0	0	1	0	0	4.3	3.6	0.5	1.4	0.5			5.4	6.8
15	1.1	1.0	0	1	1	0	4.5	4.3	3.6	4.7	2.9			6.3	6.5
16	1.1	2.0	1	0	0	2	3.8	3.6	3.6	2.0		3.6		4.5	5.6
17	0.0	1.0	0	0	0	1	4.3	3.8	2.7	2.0	0.5	4.5	0.9	6.1	6.3
18	10.6	1.0	5	5	0	1	5.0		0.5					6.8	6.8
19	0.0	1.0	0	0	0	1	4.1		0.7	2.3				5.9	6.5
20	0.0	1.0	0	0	0	1	3.6		3.6	1.8				2.0	4.7
21	1.1	0.0	0	1	0	0	5.0		0.7	0.5	0.5			6.5	6.8
22	0.0	1.0	0	0	0	1	3.6		2.0	1.8		4.5	0.7	4.5	5.4
23	0.0	1.0	0	0	0	1	4.3		3.2	3.8	1.8		2.9	6.1	6.8
24	0.0	1.0	0	0	0	1	3.4		4.1		0.5	4.5	0.9	2.1	4.7
25	1.1	0.0	0	1	0	0	5.2			0.5				6.8	6.8
26	0.0	2.0	0	0	0	2	4.7			2.5				7.0	6.8
27	1.1	0.0	0	1	0	0	4.5			0.7			0.9	5.9	6.5
28	1.1	0.0	0	1	0	0	5.0				0.5			6.3	6.8
29	1.1	0.0	0	1	0	0	5.0						3.4	6.8	6.5

NOTE:—*Results recorded as grams lactic acid per mille.*

Milk, freshly separated.

Yeast Milk—freshly separated milk enriched with yeast extract at the rate of 0.15% (5).

Yeast Litmus Milk—freshly separated milk enriched with yeast extract at the rate of 0.15% and a requisite amount of azolitmin added.

Casein Digest Broth—Nitrogen source No. 2 (1).

Discussion

The 193 cultures isolated from the two starters were Gram-positive coccus forms, and they failed to liquefy nutrient gelatin: some appeared as chains in young milk cultures, and some as pairs.

From a study of the total titratable acidity produced by the organisms in milk and in milk enriched with yeast extract after 14 days' incubation, it is seen that only six organisms show a yeast incidence, five of the organisms being found in Starter *Sye* and one in Starter *S*. These six organisms would thus be placed tentatively within the genus *Betacoccus*. The remaining 187 strains would be considered as lactic acid streptococci.

When the sugar-fermenting abilities of the organisms are considered, it is seen that the distribution of the species in the starter carried in milk enriched with yeast extract is markedly different from that in the starter carried in ordinary milk (Table I). Starter *S* is characterized by a large percentage of organisms which ordinarily would be classified as strains of *Sc. cremoris*. If those organisms that ferment salicin in addition to lactose, and as well those strains that ferment maltose or sucrose slightly are included as strains of *Sc. cremoris*, 90.4% of the organisms (85 out of 94 cultures) isolated from Starter *S*, and only 64.7% of the organisms (64 out of 99 cultures) isolated from Starter *Sye* are to be classified as strains of *Sc. cremoris*.

While only 9.6% of the organisms (9 out of 94 cultures) isolated from Starter *S* ferment the more complex carbon sources other than salicin, it is seen that 35.3% of the organisms (35 out of 99 cultures) isolated from Starter *Sye* exhibit this ability, 24.1% of the organisms (23 out of 99 cultures) fermenting lactose, salicin, maltose and starch.

The marked difference in the distribution of the species in the two starters is also to be seen when the rates of acid production, as shown by the clotting times of the organisms in milk and in yeast-enriched milk, are considered and compared with the respective sugar-fermenting abilities of the organisms.

Of the 42 cultures isolated from Starter *S* on *PMG*, only three organisms failed to clot milk or yeast milk within 48 hr., strains Nos. 9 and 13 producing a soft clot in milk in three days, and Strain No. 16 clotting yeast milk in three days and milk without enrichment in five days. From Table I it is seen that strain No. 9 ferments lactose, salicin, and sucrose; strain No. 13 ferments lactose, salicin, maltose, and starch, and that strain No. 16 ferments lactose, salicin, maltose, starch, and sucrose. It is of interest to observe also that these three strains are the only cultures obtained from Starter *S* on *PMG* that possess the ability to ferment the more complex carbon sources, and are thus not to be classified as strains of *Sc. cremoris*.

TABLE II

DISTRIBUTION OF BACTERIAL FLORA IN STARTERS

Strain No.	Per cent Starter		Starter *A*		Starter *Aye*		Lactose	Salicin	Maltose	Starch	Dextrin	Sucrose	Manni-tol	Milk	Yeast milk
	A	*Aye*	*PMG* plate 42 cultures	*PMGye* plate 47 cultures	*PMG* plate 45 cultures	*PMGye* plate 40 cultures									
1	72.0	47.0	30	34	30	10	5.2							5.9	5.9
2	10.1	22.4	4	5	8	11	5.2	1.4						5.9	5.9
3	15.7	8.2	8	6	6	1	5.2	4.7						6.1	5.9
4	0.0	2.4	0	0	1	1	4.3	4.3	4.1					3.2	4.7
5	0.0	1.2	0	0	0	1	3.8	3.2	5.0	2.0	1.1			1.4	3.8
6	0.0	3.6	0	0	0	3	5.2	3.2	4.7	4.5	4.5			6.5	6.8
7	0.0	4.8	0	0	0	4	4.7	4.1	3.8	4.3	2.9	4.1		4.3	5.4
8	0.0	1.2	0	0	0	1	5.4	3.4	4.7	3.2	2.5	1.1		7.4	7.4
9	0.0	2.4	0	0	0	2	4.5	0.5	3.6	2.5	0.9	4.5	0.5	1.4	3.8
10	1.1	1.2	0	1	0	1	5.4		2.0	0.5		2.3		5.9	5.6
11	0.0	1.2	0	0	0	1	4.7		4.1		0.7	4.1		1.4	2.9
12	0.0	1.2	0	0	0	1	5.9		4.5	4.5	4.7			7.0	7.0
13	0.0	1.2	0	0	0	1	4.1		5.0	3.6	2.9	2.7		5.4	6.3
14	0.0	1.2	0	0	0	1	4.5		5.6	2.5	1.1	5.0	2.0	4.1	4.7
15	1.1	1.2	0	1	0	1	5.2				2.5			6.1	6.3

NOTE:—*Results recorded as grams lactic acid per mille.*

Only one of the 52 organisms isolated from Starter *S* on *PMGye* exhibited a slow clotting time in milk, strain No. 15 requiring three days to clot yeast-enriched milk, and four days to clot ordinary milk. This strain ferments lactose, salicin, maltose, starch, and dextrin.

A greater proportion of slow acid-forming strains are to be found in Starter *Sye* than in Starter *S*. Fourteen out of 47 organisms picked from the *PMG* plate of Starter *Sye* required more than three days to clot milk or milk enriched with yeast extract. Two of the slow acid-forming organisms were strains of *Sc. cremoris* (strain No. 3). The other 12 cultures exhibited a marked ability to ferment the higher sugars, 11 of the organisms (strain No. 13) fermenting lactose, salicin, maltose, and starch, and the remaining organism (strain No. 15) fermenting dextrin in addition.

Twenty-one of the 52 organisms isolated from Starter *Sye* on *PMGye* were slow-clotting strains. Of these only two could be looked upon as strains of *Sc. cremoris*,—strain No. 4 and one of the two No. 6 strains. Twelve of the remaining 19 slow acid-producing cultures were identical with the 11 Starter *Sye* strains which were isolated from the *PMG* plate, and which fermented lactose, salicin, maltose, and starch. The other slow acid-forming strains are strains No. 19, 20, 16, 22, 23, and 24. Only one of these—strain No. 24—does not possess the ability to ferment starch (Table I).

Although the data reported are the results of a single experiment, nevertheless the difference in the distribution of strains in the respective starters is distinctive enough to show that yeast extract, when used as an enrichment for milk employed in the carrying of starters, induces a variation in the bacterial flora of the starter greater than that usually to be observed when the starter is sub-cultured daily under conditions maintained as constant as possible. Additional evidence in support of this conclusion is to be seen when the results obtained from the study of another starter, Starter *A*, are considered (Table II).

The addition of yeast extract to the starter milk would appear to favor the development of a larger proportion of slow acid-producing strains with the ability to ferment the more complex carbon sources. In particular it would appear to increase the percentage of starch-fermenting strains (Tables I and II).

Although we can observe and define the effect of yeast extract on the bacterial flora of the starter, it is difficult to determine the manner in which the yeast extract acts. It is possible that the influence of the yeast extract is such that the organisms usually constituting the starter acquire wider sugar-fermenting abilities, or that the growth of certain species of organisms that ordinarily fail to gain predominance are stimulated at the expense of the types usually to be found in starters propagated in milk without enrichment. The results obtained afford no conclusive evidence supporting either hypothesis. It may be observed that in the majority of cases strains showing only an indication of fermenting the more complex carbon sources were isolated from the starter carried without enrichment. It is not improbable that under the

influence of yeast extract these strains acquire to a more pronounced degree the ability to ferment these specific carbon sources, and thus account for the presence of these strains in the starter carried in yeast-enriched milk—strain No. 25 (Starter *S*) and strain No. 26 (Starter *Sye*); strain No. 12 (Starter *S*) and strain No. 13 (Starter *Sye*).

On the other hand, it may be observed that a small number of organisms possessing the ability to ferment the more complex carbon sources to a marked degree are to be found in the starter carried without enrichment (strain No. 13, Starter *S*). It is possible that the predominance of this type in starters carried in yeast-enriched milk is due to the stimulation of the growth of this type at the expense of the typical *Sc. cremoris* strains.

The results of the writers' work on the influence of yeast extract on the types of streptococci to be found in starters take on a new significance when considered in the light of the work of Whitehead and Cox (7). They have shown that in the selection of starter cultures for cheese-making, the organisms selected must have two properties: (1) they must be active acid-formers at temperatures of 20–30° C., and (2) they must be relatively unaffected in their growth and morphology at 37° C. The present writers' results indicate that the addition of yeast extract to the starter milk favors the development of a large proportion of slow acid-producing strains.

Description of Species

The principal differences between the *cremoris* and *lactis* types of Streptococci of starters are related to their sugar-fermenting abilities. According to Orla-Jensen (2), both strains ferment lactose and fail to ferment sucrose; *Sc. lactis* always ferments maltose and dextrin, and *Sc. cremoris* fails to do so, although occasionally certain strains of *Sc. cremoris* ferment maltose slightly; unlike *Sc. lactis*, which always ferments salicin, *Sc. cremoris* strains vary in their behavior in this carbon source. All strains of *Sc. cremoris* fail to ferment mannitol, and the activity of *Sc. lactis* strains in this alcohol is variable. From a study of the strains of *Sc. lactis* and *Sc. cremoris* reported upon by Orla-Jensen (2), it is seen that within each species there is considerable variation in sugar-fermenting ability. In a detailed study of the bacterial flora of spontaneously soured milk and of commercial starters, Orla-Jensen and Hansen (3) confirmed the differences between *Sc. lactis* and *Sc. cremoris* and reported the finding of several new, although closely related, species.

Although sufficient data are not available to warrant exact classification of the strains reported upon in this paper, a tentative classification based upon the sugar-fermenting abilities of the organisms would serve as a basis for comparison with the new species reported upon by Orla-Jensen and Hansen (3) and is given below.

Starter S

Strain No. 1—*Streptococcus cremoris*.
Strains Nos. 2, 3, and 4—*Sc. cremoris* fermenting salicin to a varying extent.
Strains Nos. 5 and 6—*Sc. cremoris* fermenting salicin and maltose—maltose variable.

Strain No. 7—*Sc. cremoris* fermenting salicin, with indication of dextrin-fermentation.
Strain No. 8—*Sc. cremoris* fermenting salicin, with indication of sucrose fermentation.
Strain No. 9—Streptococcus fermenting sucrose and salicin. *New strain.*
Strains Nos. 10 and 11—*Sc. mannitocremoris* (3).
Strain No. 12—*Sc. cremoris*, with indication of fermenting salicin, maltose, and starch.
Strain No. 13—Streptococcus fermenting maltose, starch and salicin. It is to be noted that this strain fails to ferment dextrin. *New species*—25 organisms.
Strain No. 14—*Sc. cremoris* fermenting salicin and starch, with indications of fermenting maltose and dextrin.
Strain No. 15—Streptococcus fermenting starch. *New strain.*
Strain No. 16—Betacoccus.
Strain No. 17—Streptococcus fermenting maltose, salicin, sucrose, and starch, with indications of fermenting mannitol and dextrin.
Strain No. 18—*Sc. cremoris* with indication of maltose fermentation.
Strain No. 19—*Sc. cremoris* with definite starch fermentation and indication of fermenting maltose—see Strain No. 26.
Strain No. 20—Betacoccus.
Strain No. 21—Streptococcus with indications of fermenting maltose, dextrin, and starch.
Strain No. 22—Betacoccus.
Strain No. 23—*Sc. lactis* fermenting starch and mannitol strongly. Resembles strain No. 157 (Orla-Jensen and Hansen (3)).
Strain No. 24—Betacoccus.
Strain No. 25—*Sc. cremoris* with indication of starch fermentation.
Strain No. 26—*Sc. cremoris* with definite starch fermentation—see strain No. 19. This strain would appear to be a new species—strain No. 306 (Orla-Jensen and Hansen (3)) ferments starch to a degree.
Strain No. 27—*Sc. cremoris* with indication of fermenting starch and mannitol.
Strain No. 28—*Sc. cremoris* with indication of dextrin fermentation.
Strain No. 29—Mannitol-fermenting strain of *Sc. cremoris*. *New strain.*

Starter A

Strain No. 1—*Sc. cremoris.*
Strains Nos. 2 and 3—*Sc. cremoris* fermenting salicin to a varying extent.
Strain No. 4—*Sc. cremoris* fermenting salicin and maltose.
Strains Nos. 5 and 6—*Sc. lactis* fermenting starch. Are identical with strain No. 15 in Starter *S*. *New Strain.*
Strains Nos. 7 and 8—*Sc. saccharolactis* (Orla-Jensen and Hansen (3)) fermenting starch. *New strain.*
Strain No. 9—Streptococcus fermenting maltose, starch, and sucrose, with indication of fermenting salicin, dextrin, and mannitol.

Strain No. 10—*Sc. cremoris* fermenting maltose and sucrose with indication of fermenting starch.

Strain No. 11—*Sc. cremoris* fermenting maltose and sucrose with indication of fermenting dextrin.

Strain No. 12—Streptococcus fermenting maltose, dextrin, and starch.

Strain No. 13—*Streptococcus lactis* fermenting starch and sucrose strongly.

Strain No. 14—*Sc. lactis* fermenting starch and sucrose.

Strain No. 15—Streptococcus with definite starch fermentation. *New strain.* It is similar to strain No. 26, Starter *S.*

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CHEESE-RIPENING STUDIES

THE INFLUENCE OF THE CONFIGURATIONAL RELATIONS OF THE HEXOSES ON THE SUGAR-FERMENTING ABILITIES OF LACTIC ACID STREPTOCOCCI[1]

A PRELIMINARY NOTE

BY OLGA OKULITCH[2] AND BLYTHE ALFRED EAGLES[3]

Abstract

The influence of the configurational relations of the hexoses on the ability of a *Streptococcus cremoris* strain to produce acid from lactose in milk and in broth has been studied.

With casein digest broth as the nitrogen source, the organism was carried by serial transfers in 10 different carbon sources; at every transfer the cultures were inoculated from the sugar broths into milk, and the clotting times of the respective milk tubes determined.

The carrying of the culture in sucrose, maltose, dextrin or starch has no influence on the acid-producing ability of the organism.

Glucose, mannose, fructose, and salicin exhibit a marked inhibiting effect on the rate and amount of acid production in milk and in lactose broth.

Although galactose and lactose fail to inhibit completely the activity of the organism, a restraining influence on acid production is to be observed. It is suggested that the inhibitory activity of glucose or one of its metabolic products may be a cause of the sudden or gradual loss of vitality in starters.

Whitehead and Cox (5) have emphasized the importance of selecting, for cheese starter cultures, streptococcus strains possessing the ability to produce acid steadily throughout the cheese-making process and to maintain this rate from day to day. In their work on starters, Whitehead and his associates (2, 3, 4, 6), have described various factors that inhibit the acid-producing ability of starter organisms.

As work progressed on the nutritive requirements of the lactic acid bacteria, the authors observed that the successive transferring of a particular *Streptococcus cremoris* strain in 2% glucose casein digest broth caused the organism to lose the ability to ferment lactose in milk or in broth culture. The work reported upon herein is a preliminary study of the influence of specific carbohydrates on the sugar-fermenting abilities of a salicin-fermenting strain of *Sc. cremoris*—strain No. 142. This organism was isolated from a commercial cheese starter and showed marked acid-producing ability in milk and in lactose broth.

Experimental

A vigorous culture of *Sc. cremoris* 142, which clotted milk overnight, was transferred from milk to sugar-free casein digest broth enriched with 0.15% yeast extract (1). Fructose, glucose, mannose, galactose, sucrose, maltose, lactose, dextrin, starch and salicin broths were inoculated with the culture after it had been incubated for 24 hr. In the preparation of the sugar broths,

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the sugar was added to casein digest broth at the rate of 2% (1). Serial transfers in each sugar broth were made at 48 hr. intervals. At every transfer, milk also was inoculated with the cultures from the sugar broths, and the time required to clot the respective milk tubes determined.

The sugar-fermenting abilities of Culture 142 in casein digest broth were determined at the beginning of the work, and at the completion of the experiment the sugar-fermenting abilities of the culture carried in each of the 10 carbon sources were also ascertained.

Discussion

Culture 142 ferments fructose, glucose, mannose, galactose, lactose and salicin, but is unable to ferment sucrose, maltose, dextrin and starch. The carrying of the culture in the last four sugars does not alter in any way the ability of the organism to form acid from lactose in milk or in broth (Tables I and II). The inhibitory influence of certain of the carbohydrates on the rate and amount of acid production in milk is to be seen, however, when the clotting times of the milk tubes inoculated with cultures from the fermentable sugar broths are considered (Table II).

TABLE I

TITRATABLE ACIDITY IN GRAMS LACTIC ACID PER LITRE

	Sucrose	Maltose	Dextrin	Starch	Lactose	Galactose	Fructose	Mannose	Salicin	Glucose
Culture 142 1st Transfer	0.0	0.0	0.0	0.0	5.9	5.4	6.8	6.8	5.0	6.5
Culture 142 after 65 transfers in										
Sucrose	0.0	0.0	0.0	0.0	5.6	4.3	6.5	6.3	5.9	6.3
Maltose	0.0	0.0	0.0	0.0	5.9	4.5	6.8	6.3	5.9	6.3
Dextrin	0.0	0.0	0.0	0.0	5.9	4.7	6.5	6.1	6.1	6.3
Starch	0.0	0.0	0.0	0.0	5.9	4.5	6.5	6.3	5.6	6.3
Lactose	0.0	0.0	0.0	0.0	5.6	4.7	6.8	6.1	5.2	6.3
Galactose	0.0	0.0	0.0	0.0	5.6	4.7	6.8	5.9	5.2	6.3
Fructose	0.0	0.0	0.0	0.0	0.0	3.8	6.5	5.9	5.2	6.1
Mannose	0.0	0.0	0.0	0.0	0.0	3.8	6.8	6.1	6.1	6.3
Salicin	0.0	0.0	0.0	0.0	0.0	3.4	6.8	6.3	6.5	6.1
Glucose	0.0	0.0	0.0	0.0	0.0	3.8	6.8	6.1	5.2	6.3

Glucose and salicin exhibit the strongest inhibitory effect. After 11 serial transfers in either of these carbon sources, the organism loses completely the ability to ferment lactose in milk or in broth. In mannose and fructose broths, a larger number of transfers are required before complete inhibition of lactose-fermenting ability is reached. The inhibitory effect is gradual in its action; an increasingly slower rate of acid production in milk at each successive transfer is to be observed; after 15 transfers in mannose, and 18 in fructose, the organism ceases to ferment lactose. The marked inhibitory influence of fructose, glucose, mannose and salicin on the acid-producing ability of the organism is also to be observed when the total titratable acidity

TABLE II

CULTURE 142—DAYS REQUIRED TO CLOT MILK

	Inoculated from									
Transfer number	Sucrose	Maltose	Dextrin	Starch	Galactose	Lactose	Fructose	Mannose	Salicin	Glucose
9	1	1	1	1	1	1	1	1	1	1
10	1	1	1	1	2	2	2	2	2	2
11	1	1	1	1	2	2	2	2	No clot	No clot
12	1	1	1	1	2	4	2	4		
13	1	1	1	1	3	4	3	5		
14	1	1	1	1	4	4	4	6		
15	1	1	1	1	3	4	3	No clot		
16	1	1	1	1	3	4	3			
17	1	1	1	1	2	4	4			
18	1	1	1	1	2	2	No clot			
19	1	1	1	1	2	4				
20	1	1	1	1	2	4				
21	1	1	1	1	2	3				
22	1	1	1	1	2	2				
23	1	1	1	1	2	2				
24	1	1	1	1	2	2				
25	1	1	1	1	2	14				
26	1	1	1	1	2	14				
27	1	1	1	1	2	14				
28	1	1	1	1	2	14				
29	1	1	1	1	2	14				
30	1	1	1	1	2	10				
31	1	1	1	1	2	10				
32	1	1	1	1	2	10				
33	1	1	1	1	2	10				
34	1	1	1	1	2	10				
35	1	1	1	1	3	10				
36	1	1	1	1	5	10				
37	1	1	1	1	5	8				
38	1	1	1	1	6	7				
39	1	1	1	1	7	7				
40	1	1	1	1	6	9				
41	1	1	1	1	4	7				
42	1	1	1	1	5	7				
43	1	1	1	1	6	10				
44	1	1	1	1	4	10				
45	1	1	1	1	3	10				
46	1	1	1	1	3	6				
47	1	1	1	1	4	6				
48	1	1	1	1	5	5				
49	1	1	1	1	5	8				
50	1	1	1	1	6	8				
51	1	1	1	1	8	8				
52	1	1	1	1	7	6				
53	1	1	1	1	6	6				
54	1	1	1	1	10	7				
55	1	1	1	1	14	7				
56	1	1	1	1	14	7				
57	1	1	1	1	10	7				
58	1	1	1	1	8	6				
59	1	1	1	1	8	6				
60	1	1	1	1	8	6				
61	1	1	1	1	8	7				
62	1	1	1	1	7	8				
63	1	1	1	1	6	6				
64	1	1	1	1	6	7				
65	1	1	1	1	6	7				

figures in the respective sugar broths are considered. Acid formation in lactose broth is completely inhibited, and a restraining influence is to be seen in the case of galactose broth (Table I).

Galactose and lactose are the only fermentable carbon sources studied which failed to induce in the organism complete loss of acid-forming power in milk. While complete inhibition was not attained after 65 transfers in either lactose or galactose, it is seen that these sugars are not without effect on the organism. For, as may be seen in Table II, the rate of acid production in milk by the culture when carried in either of these two carbon sources is subject to considerable variation; in each case the rate of acid production in milk was restrained to such an extent that at one period of the experiment 14 days were required before the organism elaborated sufficient acid to clot the milk.

Much more information is required before an hypothesis can be advanced to explain the results reported. Data obtained in the authors' laboratory indicate that when the influence of specific carbohydrates on the acid-producing ability of other closely allied strains of lactic acid streptococci is studied, a different picture presents itself.

A tentative hypothesis may be advanced to explain the influence of the different carbon sources on the acid-producing ability of Culture 142. It would appear that whenever stereoisomers of the mannitol group of aldohexoses are present in the medium (glucose and mannose), or are liberated from a more complex carbon source by the enzymatic activity of the organism, as in the case of salicin, that rapid and complete inhibition of the lactose-fermenting ability of the organism is obtained. This phenomenon is also to be observed in the case of the ketohexose fructose.

The disaccharides maltose and sucrose are not fermented by the organism and consequently no glucose or fructose is liberated. Similarly, the polysaccharides dextrin and starch are not acted on.

Galactose, an aldohexose of the dulcitol group, fails to inhibit completely the acid-producing power of Culture 142. The disaccharide lactose which yields on enzymatic hydrolysis a molecule of galactose as well as a molecule of glucose, acts in a similar manner. The rate of acid production in milk is markedly restrained, but the total titratable acidity produced in lactose broth after 14 days' incubation is maintained.

Is the non-ability of galactose to induce a complete loss of acid-forming power from lactose related to the fact that in galactose the middle pair of asymmetric groups are symmetrically arranged, in contrast with the configuration of the mannitol group of hexoses in which the middle pair of asymmetric groups are diagonally situated? The question arises whether the inhibitory power of the carbohydrates may be more intimately connected with the detailed structure of the sugar. Is the inhibitory action of a specific sugar related to the configuration of the sugar as revealed by the nature of the saccharic acid which it yields on oxidation? If such a relation exists, one would expect that idose and gulose of the mannitol group, and talose and

altrose of the dulcitol group, would completely inhibit the acid-producing ability of the organism, as do glucose and mannose. One would also expect that the action of allose would be similar to that of galactose. Work on this aspect of the problem is now proceeding.

The fact that the propagation of Culture 142 in certain specific carbohydrate broths induces in the organism an inability to ferment lactose, is of interest from the standpoint of the physiology of the organism. The question arises as to how the loss of lactose-fermenting ability is induced in the culture. A possible explanation of the phenomenon is that a product of the metabolic activity of the organism, when grown in a specific carbohydrate, inhibits the action of the enzyme lactase; or that this product serves to alter the metabolism of the organism in such a manner that lactase is no longer elaborated.

Whatever may be the explanation, the results indicate that one of the causes of the sudden or the gradual loss of acid-forming ability in starters may be the inhibitory activity of glucose itself, or due to one of the metabolic products arising from glucose during the course of the fermentation of lactose in the starter milk.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XI. TWO NEW ALKALOIDS, CORLUMINE AND CORLUMIDINE, AND THEIR CONSTITUTIONS[1]

By Richard H. F. Manske[2]

Abstract

A new alkaloid, *corlumine*, has been isolated from *Corydalis scouleri*, *C. sibirica* and *Dicentra cucullaria*. Chemical examination disclosed its isomerism with adlumine with which, furthermore, it is structurally identical. It differs from the latter only in the disposition of the substituents about the two asymmetric C-atoms, but it is not the optical antipode of adlumine. *Corlumidine* is O-desmethyl corlumine and has been found only in *C. scouleri*, and on methylation with diazomethane yields corlumine. The free hydroxy-group is probably present in the 7-position of the isoquinoline nucleus.

The further chemical examination of Fumariaceous plants has disclosed two new phthalide isoquinoline bases. Though bicuculline (2, 3) has now been isolated from nine different species, the closely related adlumine (4) has been found only in *Adlumia fungosa*. The unknown tetramethoxy analogue is probably present in *C. aurea*, but only sufficient for an analysis has thus far been obtained. It was, therefore, somewhat unexpected to encounter an alkaloid, which was clearly a phthalide isoquinoline base, isomeric with adlumine and hydrastine but identical with neither. This base, for which the name *corlumine* (the first syllable is derived from *Corydalis* and the remaining two from adlumine, owing to its close relation to the latter) is now proposed, has been isolated thus far from only three plants, namely, *Corydalis scouleri*, *C. sibirica* and *Dicentra cucullaria*. Owing to the extreme difficulty with which the first crystal nucleus was obtained, the author anticipates its further isolation from some refractory mother liquors from other plants. It is proposed to place on record in the near future several communications dealing with some of the subjects mooted above.

The structural identity of corlumine with adlumine (5) was placed beyond doubt by its hydrolytic oxidation with dilute nitric acid. The same products were obtained and their identity was established, as recorded in the experimental section. It is obvious, therefore, that the two alkaloids differ only in the disposition of the substituents about the two asymmetric C-atoms, formula (I) applying to both bases. Perhaps the best known and probably the only strictly analogous case of optical isomerism in alkaloids is that of ephedrine and pseudo-ephedrine.

A second alkaloid, for which the name *corlumidine* is now proposed, has also been isolated from *C. scouleri*. It is phenolic and this property obscured for a time its relation to the phthalide bases. On methylation with diazomethane, however, it readily yielded corlumine, so that only two possible

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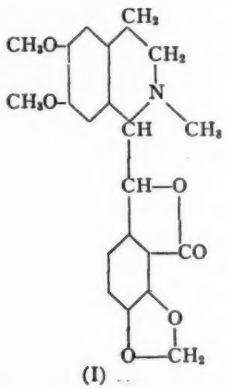
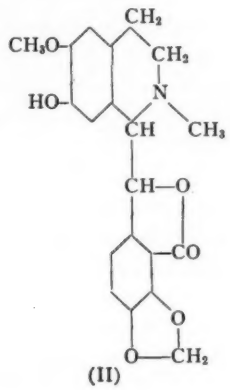
structures come under consideration, the most probable of which (II) is based upon a knowledge of the other bases in the same plant. In this connection, it may be permissible to anticipate a communication dealing with *C. scouleri* by announcing the isolation of Knörck's alkaloid (1, 6) (2 : 9-dihydroxy-3 : 10-dimethoxy-tetrahydro-protoberberine) from this plant in which the hydroxyl in the isoquinoline nucleus is in the same position as in (II).



(I)



(II)

Experimental

Hydrolytic Oxidation of Corlumine

The procedure detailed in the case of adlumine was followed without modifications. The aminoaldehyde (lodal) melted at 124° C.* either alone or in admixture with a specimen prepared from adlumine. Treatment of the above with alkali (Cannizzaro) and separation of the products yielded 2-methyl-6 : 7-dimethoxy-tetrahydroisoquinoline (m.p. 84° C.) and the corresponding 1-keto-derivative (m.p. 126° C.). No depression in melting point occurred when these substances were mixed with the corresponding compounds obtained from adlumine.

The acidic fragment was isolated in the usual way, and it melted at about 150° C. The melting point was not depressed when it was admixed with 2-carboxy-3 : 4-methylenedioxy-benzaldehyde prepared from bicuculline. It was observed that the heating of this aldehyde with aqueous alkali yielded a mixture of 3 : 4-methylenedioxy-phthalide (m.p. and mixed m.p. 232° C.) and 3 : 4-methylenedioxy-phthalic acid, which alone or admixed with an authentic specimen melted at 202° C. with anhydride formation, some sintering taking place several degrees lower.

This procedure is analogous to the conversion of opianic acid by alkali into meconine and hemipinic acid, and for identification is preferable to reduction with sodium amalgam. Owing to the virtual insolubility of the phthalide in cold water, the two products are easily separable.

**All melting points are corrected.*

Methylation of Corlumidine

A suspension of 0.2 gm. of corlumidine (m.p. 236° C.) in chloroform-methanol was treated with an ethereal solution of diazomethane. Evolution of nitrogen progressed smoothly and the sparingly soluble base gradually dissolved. After 24 hr. the excess diazomethane and the organic solvents were evaporated. The residue was dissolved in dilute hydrochloric acid and the filtered solution cautiously basified with aqueous potassium hydroxide, and the liberated base extracted with ether. The washed solution was freed of solvent; the residue dried at 60° C. and dissolved in a small volume of methanol. In the course of several days the non-phenolic base crystallized in colorless prisms which melted at 158° C., and this melting point was not changed when the base was admixed with a specimen of corlumine. A crystal of corlumine when added to a supersaturated methanolic solution of the above induced immediate crystallization.

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THE REACTION ALUMINIUM OXIDE–CARBON–CHLORINE[1]

By Norman M. Stover[2] and Clinton Constantinescu[3]

Abstract

The reaction aluminium oxide–carbon–chlorine has been investigated and found to produce aluminium chloride, oxygen and carbon dioxide. This occurred when a mixture of aluminium oxide and carbon was heated either in a stream of chlorine or in a static atmosphere of chlorine. No carbon monoxide was obtained when a stream of chlorine was used, but small amounts were formed in a static atmosphere of chlorine. The temperature at which reaction started, as shown by the formation of a sublimate of aluminium chloride in the reaction tube, decreased as the proportion of carbon to aluminium oxide increased. In a number of experiments, less carbon was consumed than should have been for the amount of aluminium oxide that reacted, if it be assumed that carbon dioxide, rather than oxygen, was a primary product. From the results obtained, the writers believe that oxygen is a primary product of the reaction, while carbon dioxide is a secondary product, the carbon acting primarily as a catalyst.

In experiments with tungstic oxide, also, oxygen was produced, but, contrary to the findings of other investigators, carbon dioxide was also formed.

Introduction

A recent investigation carried out by Sears and Lohse (4) on the chlorination of mixtures of tungstic oxide and carbon indicated that carbon played the role of catalyst. This conclusion was reached partly because, under certain conditions of experiment, it was found that: (i) oxygen was present in the gaseous products of the reaction; (ii) very little, if any, loss of carbon occurred during reactions carried out in a stream of chlorine; (iii) reactions took place at lower temperatures when carbon was present than when it was absent; (iv) and the reactions took place at increased rates when the proportion of carbon was increased. The results indicated the reaction to be:

$$2WO_3 + 2Cl_2 \longrightarrow 2WO_2Cl_2 + O_2. \qquad (1)$$

The majority of textbooks on inorganic chemistry represent the chlorination of mixtures of carbon and metallic oxides as producing carbon monoxide or carbon dioxide. Consequently, the present writers thought it might be of interest to repeat the work of Sears and Lohse, but using other metallic oxides. Aluminium oxide was chosen to start with, partly because this material and this reaction are used in the commercial production of anhydrous aluminium chloride.

The mechanism of the chlorination of mixtures of aluminium oxide and carbon is often represented by the equation

$$6Cl_2 + 2Al_2O_3 + 3C \longrightarrow 4AlCl_3 + 3CO_2. \qquad (2)$$

If, in this reaction, carbon is a catalyst, then oxygen should be one of the products and the equation should be

$$2Al_2O_3 + 6Cl_2 \xrightarrow{(C)} 4AlCl_3 + 3O_2. \qquad (3)$$

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Since the reaction occurs at temperatures of about red heat, there is the possibility that the hot carbon may be attacked by any oxygen liberated, with the formation of carbon dioxide or carbon monoxide. If, however, a stream of chlorine were maintained, the oxygen would probably be swept out of contact with the carbon, and free oxygen would be obtained. It would be expected that in a static atmosphere any free oxygen liberated would react with the excess carbon, with the formation of an oxide of carbon.

The action of chlorine alone on aluminium oxide was found by Spitzin (5) to begin at about 800° C. He states that carbon has no effect on the temperature at which the reaction begins, and that its accelerating effect is probably due to its reaction with the oxygen produced in the main reaction, thus preventing equilibrium from being established.

According to Kangro and Jahn (1), aluminium oxide must be heated to 1200° before chlorine will react appreciably with it.

Treadwell and Gyger (6) studied the action of carbon on aluminium oxide at temperatures as high as 1900° C. and concluded that at a temperature of 1000° C., or lower, no action took place.

A number of investigations (2, 3, 7) have been conducted on the combined action of chlorine and carbon on aluminium oxide. In some of these, carbon monoxide was shown to be the gaseous product, while in others carbon dioxide was produced. There thus seems to be considerable difference of opinion as to the nature of this reaction, and also as to the gaseous products formed.

Materials

Carbon

It was felt that the use of wood charcoal would introduce mineral impurities that might have some effect on aluminium oxide in the presence of chlorine. Indeed, it was found that a considerable amount of sublimate was formed when "Norite" charcoal was heated to 640° C. in chlorine. Pure sugar charcoal was finally selected for use. It was made by treating 120 gm. of pure cane sugar, dissolved in 90 cc. of water, with 120 cc. of concentrated sulphuric acid. The precipitated carbon was boiled for two hours in concentrated sulphuric acid, then washed with hot water until free from sulphate, and finally filtered and dried at 125° C. The dry carbon was pulverized and heated to 760° C. in nitrogen. This carbon, on complete oxidation, left no visible residue.

Aluminium Oxide

This was prepared by treating a solution of c.p. $AlCl_3.6H_2O$ with excess ammonium hydroxide, washing the precipitated aluminium hydroxide free from chloride, drying and heating to a bright red heat.

An intimate mixture of aluminium oxide and carbon was also made by precipitating aluminium hydroxide in the presence of carbon prepared as described above. This mixture, after thorough washing and drying, was heated to 850° C. in an atmosphere of nitrogen. Two such mixtures were so made as to contain different ratios of carbon to aluminium oxide.

Chlorine

In preliminary experiments it was found that when pure carbon was heated in the presence of chlorine drawn from a cylinder of the commercial liquid, the carbon gradually disappeared. Upon analysis, this chlorine was found to contain approximately 3% by volume of oxygen, as well as carbon dioxide and an inert gas (presumably nitrogen). The presence of oxygen prevented the use of tank chlorine during the investigation. Hence, for the main part of the work, chlorine was generated by dropping c.p. concentrated hydrochloric acid onto solid c.p. potassium permanganate.

Confining Solution

To collect, and store for analysis, furnace gases consisting of mixtures of chlorine, carbon dioxide, oxygen and carbon monoxide, a 20% solution of sodium sulphate containing 5% of sulphuric acid was used. "Nujol" was tried, but was found to be attacked by chlorine.

Chlorine appeared to exert no action upon this confining solution, as indicated by no change in a sample of this gas confined over the solution for several days. Moreover, samples of mixtures of carbon dioxide, oxygen, carbon monoxide and chlorine gave the same analyses when analyzed after confinement for several hours as they did immediately after mixing. Since, in the various experiments, the off-gases from the reaction tube were neither stored over the confining solution for periods longer than an hour at the most, nor exposed to direct sunlight, it seems safe to assume that none of the oxygen obtained in the runs was produced by the action of chlorine on the water of the confining solution.

Apparatus

The gas-analysis apparatus was patterned after the Orsat apparatus and equipped with a Pettersson pressure compensator. The carbon dioxide pipette contained 40% potassium hydroxide solution. Potassium pyrogallate solution was used for oxygen absorption, while for carbon monoxide two absorption pipettes were employed, one containing acid cuprous chloride solution (with copper wire spirals present), the other cuprous sulphate—β-naphthol mixture in sulphuric acid. These solutions were made up according to directions in "Methods of the Chemists of the United States Steel Corporation for the Sampling and Analysis of Gases."* The method adopted in analyzing the gases was that commonly used with absorption pipettes and an Orsat apparatus.

The main apparatus consisted of the following pieces connected in series by gum rubber tubing in the order mentioned: a chlorine generator (solid potassium permanganate and concentrated, c.p. hydrochloric acid were used); a wash bottle containing saturated potassium permanganate solution to remove any hydrogen chloride gas carried over from the generator; a wash bottle containing concentrated sulphuric acid; a drying tower containing

*Pages 36-40. Third edition. 1927.

anhydrous calcium chloride; a transparent quartz tube in a three-unit electric combustion furnace, the tube being equipped with a chromel-alumel thermocouple sheathed in quartz.

Procedure

Weighed quantities of aluminium oxide and carbon were mixed in a porcelain boat and placed in the furnace tube adjacent to the thermocouple.

After the apparatus was assembled, it was flushed with oxygen-free nitrogen and then with chlorine from the generator. After about one hour 1000 cc. of exit gas was collected, shaken with mercury until all chlorine was removed, and any residual gas analyzed for carbon dioxide and oxygen. When these two gases were shown to be absent, or nearly so, the furnace was heated quickly until a sublimate of aluminium chloride began to form. Soon thereafter 1000 cc. of exit gas was collected, chlorine removed as in the blank, and any remaining gas analyzed for carbon dioxide, oxygen and carbon monoxide. The time consumed in collecting the 1000 cc. samples of gas averaged about five minutes, while the furnace temperatures at which samples were withdrawn ranged from 644 to 880° C. Sometimes several samples of gas were collected at different temperatures during the same run. After one or more samples had been collected, the reaction tube was allowed to cool while pure nitrogen was replacing the chlorine. When cool, the boat with residue was weighed. Any carbon left was burned off in a current of oxygen and the boat re-weighed. The weights of aluminium oxide and carbon consumed during the run could thus be calculated.

Runs were made with different ratios of aluminium oxide to carbon, and also with the chlorine in a steady current and in a static condition. In some cases the aluminium oxide and carbon were mixed after weighing separately, while in other cases more intimate mixtures were made by precipitating aluminium hydroxide in the presence of carbon in predetermined proportions.

Several runs were made with c.p. tungstic oxide instead of aluminium oxide, in an attempt to duplicate the work of Sears and Lohse (4) and as a basis for comparing results obtained when aluminium oxide was used.

Results

The results of the runs are shown in Tables I, II, III and IV. Table I shows results that were typical of runs made with mixtures of aluminium oxide and carbon in a stream of chlorine, the mixtures being made after weighing the ingredients. Table II contains results obtained when the specially prepared, intimate mixtures were used in a stream of chlorine. As will be noted, two mixtures containing different proportions of aluminium oxide and carbon were used. Table III gives results for a static atmosphere of chlorine, both for coarse and intimate mixtures. Table IV represents the results of a brief attempt to duplicate the work of Sears and Lohse (4), tungstic oxide instead of aluminium oxide being used.

It will be observed that in several instances a number of samples were taken during the run.

TABLE I

No. of run	Weight Al_2O_3, gm.	Weight C, gm.	Ratio Al_2O_3 to C	Blank: 1000 cc.				Temp. first sublimate, °C.	Sample of exit gases: 1000 cc.					
				Temp. of blank, °C.	Residue, cc.	CO_2 cc.	O_2 cc.		Temp. at collection, °C.	Time to collect, min.	Residue, cc.	CO_2 cc.	O_2 cc.	CO cc.
8	0.7041	0.1706	4.1	20	5.7	0.4	1.1	650	660–680	8	51.8	46.6	1.7	0.0
11	0.7593	0.2692	2.8	20	3.0	0.3	0.8	644	644–664	7	56.9	53.0	2.3	0.0
									702–726	6	20.1	13.8	2.8	0.0
12	0.5583	0.1965	2.8	20	2.0	0.0	0.4	640	644–664	5	23.5	18.3	2.5	0.0
									676–690	3	3.3	0.5	1.0	0.0
13	0.1725	0.0650	2.7	20	4.7	0.4	2.2	641	662	4	76.2	9.3	61.5	0.0
14	0.1442	0.0537	2.7	20	8.6	0.5	1.1	659	688	2	2.8	0.5	1.2	0.0
15	0.5882	0.1854	3.2	20	4.7	0.5	0.6	646	654–673	3	16.9	13.7	0.6	0.0
17	0.5318	0.2189	2.4	20	1.1	0.1	0.3	630	846–857	5.5	2.7	1.1	0.6	0.0
									871–872	4.5	1.6	0.6	0.4	0.0
5	0.1262	0.0098	12.9	20	3.9	0.2	0.5	654	700	7	24.3	3.7	6.2	0.1
18	0.5083	0.0336	15.1	20	1.8	0.3	0.5	692	726	4.5	8.0	2.4	3.7	0.0
									726–748	5.5	7.4	1.9	3.6	0.0
									795	3	2.2	0.6	0.7	0.0
20	0.3985	0.0301	13.2	20	1.7	0.3	0.6	696	722–746	7	10.7	4.1	4.1	0.0
									758–762	5	5.7	2.0	2.5	0.0
21	0.6636	0.0502	13.2	20	0.9	0.0	0.3	688	860–864	4	4.8	0.4	1.3	0.0
22	0.4321	0.0339	12.7	20	1.3	0.1	0.4	692	698–712	6	12.2	2.6	4.0	0.0
2	0.6818	—	—	20	1.6	0.1	0.5	—	660	4	1.3	0.4	0.3	0.0
3	0.5944	—	—	20	1.1	0.4	0.3	—	650	4	2.4	0.0	0.6	0 0
4	—	0.6793	—	20	11.1	0.6	1.2	—	510–520	6	3.3	0.5	1.1	0.0

TABLE II

No. of run	Weight mixture Al_2O_3 and C, gm.	Ratio Al_2O_3 to C	Blank: 1000 cc.				Temp. first sublimate, °C.	Sample of exit gases: 1000 cc.					
			Temp. of blank, °C.	Residue, cc.	CO_2 cc.	O_2 cc.		Temp. at collection, °C.	Time to collect, min.	Residue, cc.	CO_2 cc.	O_2 cc.	CO cc.
23	0.5708	11.5	20	2.0	0.3	0.4	672	700	3.5	3.6	0.6	0.9	0.0
								750–760	4	5.8	1.6	1.0	0.0
24	0.5668	11.5	20	1·2	0.4	0.6	670	700	6	10.8	7.7	2.1	0.0
								750–760	6	9.6	6.2	2.2	0.0
								840–850	6.5	13.9	7.1	1.6	0.0
25	0.6531	11.5	20	0.7	0.0	0.2	674	700	5	8.3	4.7	3.3	0.0
								750	5	12.3	5.4	2.1	0.0
								840	5	10.5	4.3	1.2	0.0
26	0.6086	2.7	20	1.9	0.5	0.5	646	688	5	48.1	36.7	3.1	0.1
								735	5	20.3	10.8	3.2	0.0
								840	4	14.3	4.6	3.6	0.0
27	0.6277	2.7	20	1.5	0.7	0.6	649	680	6.5	35.3	30.1	1.9	0.0
								740	6	31.5	13.1	4.2	0.0
								840	4.5	17.1	5.4	2.2	0.0
28	0.6209	2.7	20	1.0	0.2	0.4	650	690	5	53.5	39.9	2.7	0.0
								740	3	9.7	6.0	0.9	0.0
								850	5	22.0	7.8	2.8	0.0

TABLE III

No. of run	Weight mixture, gm.	Weight Al_2O_3, gm.	Weight C, gm.	Ratio Al_2O_3 to C	Blank: 1000 cc.				Temp. system closed, °C.	Temp. first sublimate, °C.	Sample of exit gases: 1000 cc.						
					Temp. of blank, °C.	Residue, cc.	CO_2 cc.	O_2 cc.			Temp. of reaction, °C.	Time of reaction, min.	Temp. sample flushed, °C.	Residue, cc.	CO_2 cc.	O_2 cc.	CO cc.
29	—	0.4493	0.0312	14.4	20	3.1	0.2	0.6	650	710	770	20	450	24.1	19.1	1.7	0.1
30	—	0.4523	0.0316	14.3	20	9.5	0.5	0.9	600	699	720	20	350	20.6	15.2	1.0	0.1
31	—	0.4588	0.0379	12.1	20	3.2	0.3	0.6	650	706	730	20	250	23.2	17.2	2.5	0.0
32	—	0.3823	0.1079	3.5	20	1.7	0.2	0.3	637	664	690	20	250	34.8	33.0	0.6	0.0
33	—	0.4794	0.1740	2.8	20	2.4	0.2	0.6	620	634	700	20	275	47.4	40.2	2.3	0.5
34	—	0.5142	0.1958	2.6	20	3.5	0.6	0.5	630	630	680	20	200	45.3	24.0	3.3	0.7
35	0.6373	—	—	11.5	20	1.1	0.3	0.4	650	700	750	20	250	37.1	33.4	1.1	0.0
36	0.6030	—	—	11.5	20	2.1	0.6	0.8	675	696	750	20	250	35.4	33.0	0.5	0.0
37	0.6121	—	—	11.5	20	1.4	0.3	0.4	670	694	730	20	325	41.2	36.9	1.4	0.1
38	0.5988	—	—	2.7	20	0.8	0.0	0.3	610	652	680	20	200	42.1	31.5	2.9	3.7
39	0.5844	—	—	2.7	20	1.4	0.5	0.5	625	655	750	20	350	46.2	29.9	1.8	3.4
40	0.6104	—	—	2.7	20	1.2	0.5	0.2	640	654	700	20	220	53.9	39.9	3.3	2.9

TABLE IV

No. of run	Weight WO_3, gm.	Weight C, gm.	Ratio WO_3 to C	Blank: 1000 cc.				Temp. first sublimate, °C.	Sample of exit gases: 1000 cc.					
				Temp. of blank, °C.	Residue, cc.	CO_2 cc.	O_2 cc.		Temp. at collection, °C.	Time to collect, min.	Residue, cc.	CO_2 cc.	O_2 cc.	CO cc.
46	0.8826	0.0326	27.1	20	1.7	0.3	0.4	350	520	4	15.4	10.1	1.9	0.0
									640	4	1.6	0.3	0.7	0.0
									750	4	1.8	0.3	0.4	0.0
47	1.0415	0.0650	16.1	20	1.0	0.5	0.2	350	500–520	4	27.4	23.1	1.5	0.0
									580	4	4.2	0.6	1.1	0.0
48*	1.1494	0.0763	15.1	20	1.7	0.5	0.4	280	460–480	3	22.8	18.5	1.4	0.0
49*	1.1798	0.0651	18.1	20	0.5	0.0	0.2	280	540–560	3	30.0	28.5	0.6	0.0

* *"Norite" used in place of c.p. sugar carbon.*

Ratios of ingredients in the mixtures are given as ratios by weight.

The results, which the authors believe point to a catalytic role for carbon in the reaction, may be summarized as follows:

Carbon dioxide and oxygen were both obtained in all runs in the off-gases from the reactions. The amounts of free oxygen obtained were greater than the amount of oxygen present in the in-going gas, despite the presence of excess carbon. In general, for a given ratio of aluminium oxide to carbon, a greater proportion of carbon dioxide to oxygen was obtained when relatively large amounts of mixtures were used than when small amounts were used. The fact that oxygen was always obtained indicates that the main reaction was probably that expressed by Equation (3). The increase in proportion of carbon dioxide with increase in amount of mixture was no doubt due to a secondary reaction in which some of the liberated oxygen reacted with the hot, excess carbon present. This condition was found to exist both when the chlorine was used in a steady stream and as a static atmosphere.

No carbon monoxide was obtained in runs made when a stream of chlorine was used, but definite amounts were obtained in a static atmosphere of chlorine.

Further, it was found that the temperature at which a sublimate of aluminium chloride first appeared decreased, in general, as the ratio of aluminium oxide to carbon decreased (*i.e.*, as the proportion of carbon to aluminium oxide increased).

Finally, in many of the runs, but not in all, it was observed that less carbon was actually consumed than that required to form carbon dioxide with the oxygen of the aluminium oxide that had reacted, according to Equation (2). The amounts of aluminium oxide and carbon consumed during the runs were not included in the tables because the reactions were not run to completion, and, further, no attempt was made to collect all the gases produced in even the partial runs.

In the experiments with tungstic oxide, oxygen was formed in every case when a flow of chlorine was used, but, whereas Sears and Lohse (4) obtained no carbon dioxide, the present authors obtained good yields of this gas. This may possibly have been due to the different temperatures at which the off-gases were collected.

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A STUDY CONCERNING THE KINETICS OF THE SULPHITE PROCESS[1]

By A. J. Corey[2] and O. Maass[3]

Abstract

Delignification rates of spruce wood chips and wood-meal have been investigated under carefully controlled conditions at temperatures ranging from 100° to 140° C. The rates are shown to be in only approximate agreement with the monomolecular law, but the change in the rate of delignification with temperature obeys the equation of Arrhenius.

Introduction

Our knowledge of the kinetics of the process whereby paper pulp is produced by the treatment of wood in calcium bisulphite solutions is due chiefly to the investigations carried out by Stangeland (9) and Yorston (10, 11). Stangeland measured the rates of solution of spruce wood-meal "incrustants" in sulphite liquor at various temperatures, and reported that the rate of solution of the "incrustants" obeyed the laws of a first order reaction. The "incrustants" included all substances present in the wood except those determined as Cross and Bevan cellulose. Stangeland explained his results by assuming an initial very rapid sulphonation, followed by an acid hydrolysis the rate of which governed the over-all rate of the reaction. This is similar to the mechanism suggested by Hägglund (6).

Yorston determined the rates of delignification of various species of coniferous woods in bisulphite solutions at 130° C., and found that the rate of lignin removal in each case deviated considerably from the rate required by a first order reaction. The experimental results also indicated that the sulphonation stage of the reaction proceeds at such a rate as to exert some influence upon the measured delignification rate, but the exact relation between the rates of sulphonation and hydrolysis of the lignin was not discovered.

During the course of an investigation into some phases of the sulphite process, considerable data have been obtained on the rate of delignification of wood in bisulphite solutions. Experiments in which spruce wood chips were used have been carried out at 120°, 130° and 104° C. The rapid method of penetration developed in this laboratory (4) was employed. Spruce wood-meal also was cooked at 100°, 110°, 120°, 130° and 140° C., but a complete delignification curve was determined only at the last temperature. Wood chips, 2 cm. in length, were prepared. The wood-meal was screened, and that fraction which passed a 40 mesh sieve, but was retained by a 100 mesh sieve, was employed in the experiments. The chip samples used in the different series of cooks were not all obtained from the same log, so that no comparisons of the reaction rates at different temperatures can be made.

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However, the wood-meal samples were identical in each case, and the temperature coefficient of the process could be determined. The initial concentration of the cooking liquor used in these experiments was always about the same for each run: namely, total SO_2, 5.10; free SO_2, 3.90; combined SO_2, 1.20%.

Two types of apparatus were employed. The chips were cooked in the penetration cell described in an earlier paper (2), and the wood-meal, in glass lined, bronze, bomb-type digesters. When a 6 gm. sample was cooked in the penetration apparatus, the liquor to wood ratio was about 10 : 1, and about 30 : 1 when the bombs were employed.

In the cooking experiments, performed in the penetration cell, it was customary to raise the temperature gradually to the maximum cooking temperature in 30 min., after which time it was maintained constant until the cook was finished. A preliminary test run on the wood used in the series at 130° C. showed that evacuation of the cell for 30 min., and the introduction of the cooking liquor into the wood under a pressure of seven atmospheres, was sufficient to cause complete penetration of the wood immediately. No "burning" occurred when the cell was quickly immersed in an oil bath heated to 130° C. This procedure was followed only in the series at 130° C., but it offers a striking illustration of the efficiency of this method for securing complete and rapid penetration. No penetration period was required when the wood-meal was cooked. The bath was heated to about 5° C. above the desired temperature, the bombs were then immersed, and the temperature allowed to fall to the desired value. At suitable intervals a bomb was removed, and the contents was tested to determine the progress of the reaction. There was no gas relief during cooking.

In the tabulated results the lignin remaining in the pulp, expressed as a percentage of the original wood sample, is designated as the residual lignin. The yield of carbohydrate is determined as the difference between the yield of pulp and the percentage of residual lignin.

TABLE I

SPRUCE WOOD CHIPS COOKED IN BRONZE BOMBS AT 100° C.*

Length of cook, hr.	Yield of pulp, %	Yield of carbohydrate, %	Lignin in pulp, %	Residual lignin, %
8	85.7	69.3	19.2	16.4
16	78.4	66.1	15.7	12.3
24	71.5	65.7	8.13	5.82
40	62.4	58.5	6.27	3.92
56	57.8	56.2	2.70	1.56
72	55.6	54.5	2.00	1.13
96	54.0	53.2	1.44	0.78
108	53.1	52.3	1.73	0.83
120	51.0	50.3	1.45	0.74
132	50.5	50.8	1.46	0.74
150	49.3	48.6	1.41	0.69
176	47.4	46.8	1.38	0.65

Lignin in the wood, 29.1%.

**The above results, obtained by Dr. R. de Montigny, are included here to show the extent to which wood may be delignified at the relatively low temperature of 100° C.*

TABLE II

SPRUCE WOOD CHIPS COOKED IN THE PENETRATION CELL AT DIFFERENT TEMPERATURES

Length of cook, hr.	Yield of pulp, %	Yield of carbohydrate, %	Lignin in pulp, %	Residual lignin, %
A. Wood density, 0.35; lignin content, 29.9%. Temp. 120° C.				
2	79.0	60.0	24.1	19.0
4	69.0	55.3	19.9	13.7
6	59.8	53.5	10.45	6.25
8	55.2	51.4	6.92	3.82
10	50.2	48.3	3.75	1.89
12	50.4	49.1	2.56	1.28
14	46.0	44.9	2.47	1.13
20	45.7	44.7	2.22	1.01
B. Wood density, 0.35; lignin content, 32.6%. Temp. 130° C.				
0.5	91.4	61.0	33.3	30.5
1	85.2	57.4	32.6	27.8
2	79.8	60.2	24.4	19.5
3	66.4	52.0	21.7	14.4
4	62.7	52.3	16.5	10.3
5	57.7	52.6	8.73	5.0
6	54.0	50.0	7.36	4.0
8	51.2	48.7	5.30	2.5
10	50.2	49.1	2.15	1.08
C. Wood density, 0.35; lignin content, 29.9%. Temp. 140° C.				
1	70.0	53.3	23.9	16.7
2	56.7	49.5	12.7	7.2
3	52.7	48.5	7.96	4.2
4	47.3	45.5	3.85	1.82
5	47.0	46.1	2.01	0.94
D. Wood density, 0.33; lignin content, 30.5%. Temp. 140° C.				
0.5	85.9	61.3	28.7	24.7
1.5	63.3	55.8	14.4	9.4
3	53.2	49.3	7.35	3.91
5	46.3	45.0	2.55	1.17

TABLE III

SPRUCE WOOD-MEAL COOKED IN BRONZE BOMBS AT 140° C.

Length of cook, hr.	Yield of pulp, %	Yield of carbohydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur	
					% of pulp	% of lignin
0.5	82.7	61.4	25.8	21.3	0.703	2.72
1	68.7	55.0	20.1	13.7	0.967	4.81
2	54.1	49.2	9.13	4.94	0.763	8.37
3	47.4	45.9	3.12	1.48	0.331*	13.4*
4	45.8	45.2	1.43	0.65	0.258	18.0
5	44.4	44.0	0.90	0.40	0.208	23.1

Wood density, 0.34; lignin content, 29.0%.

**Sulphur values taken from another cook made under identical conditions.*

Apparent values of 13 to 23% sulphur in the low residual lignins may be due to systematic analytical error, as some lignin may be soluble in sulphuric acid or there may be traces of sulphur not combined with lignin.

TABLE IV

VELOCITY CONSTANTS OF SULPHITE DELIGNIFICATION

Wood samples		Temp., °C.	Velocity constant, k
Form	Density		
Chips	—	100	0.06
Chips	0.35	120	0.31
Chips	0.35	130	0.35
Chips	0.35	140	0.70
Chips	0.33	140	0.69
Wood-meal	0.34	140	0.98

In order to determine the temperature coefficient of the reaction, two cooks were carried out for suitable lengths of time at each of the temperatures 100°, 110°, 120° and 130° C. The wood-meal was identical with that used in the series at 140° C. (Table III), so that the coefficient was determined over the range from 100° to 140° C.

TABLE V

SPRUCE WOOD-MEAL COOKED IN BRONZE BOMBS AT VARIOUS TEMPERATURES

Temp., °C.	Time, hr.	Yield of pulp, %	Yield of carbohydrate, %	Lignin in pulp, %	Residual lignin, %	Velocity constant, k
100	20	65.1	57.0	12.4	8.09	
100	30	58.5	54.0	7.6	4.45	0.063
110	15	54.2	51.0	5.88	3.18	
110	20	51.3	49.8	2.88	1.47	0.149
120	6	58.5	51.9	11.2	6.57	
120	12	49.0	48.9	1.96	0.96	0.266
130	3	59.5	52.1	12.5	7.43	
130	6	47.7	46.4	2.67	1.26	0.490
140	(see Table IV)					0.986

Discussion

If the delignification reaction of the sulphite process proceeds at the rate of a first order reaction, its velocity is described by the equation,

$$2.303 \log \frac{Lo}{L} = kt.$$

Hence a linear relation would exist between the logarithm of the residual

lignin and the time of cooking. In Fig. 1 these two values are plotted for the different temperature series in which chips were used. The curves show definite deviations from a straight line relation and are thus in complete agreement with the results of Yorston (11), particularly the more pronounced deviation occurring during the first few hours of the reaction.

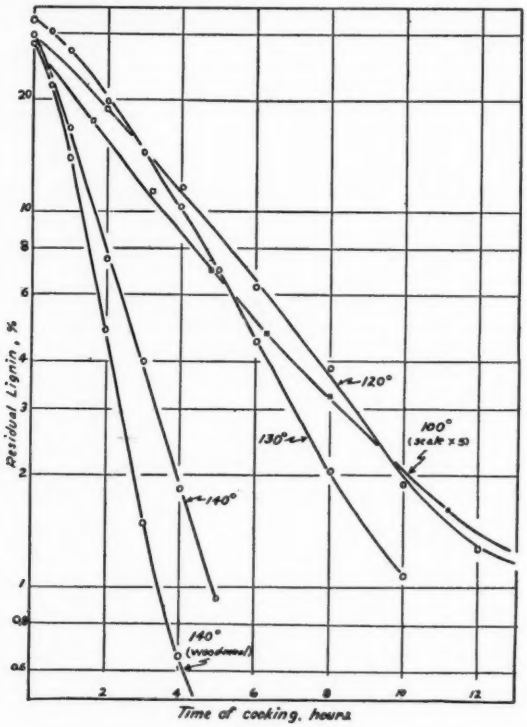

FIG. 1

A possible explanation for the fact that Stangeland (9) did not observe this phenomenon may be found in the work of Bray and Andrews (1). These workers determined the ratios between the quantities of lignin and carbohydrate that had gone into solution after given times of digestion. It was found that the ratio of dissolved lignin to dissolved carbohydrate was 0.90 during the first seven hours. After nine hours the ratio had increased to 1.30, and it continued to increase so that the final average ratio was 1.77. It will be remembered that Stangeland measured, not the rate of delignification, but the rate of "incrustant" removal. This included all carbohydrate substances in the wood other than Cross and Bevan cellulose. Bray and Andrews have shown that, in the early part of the cooking process, some carbohydrate substances are dissolved out faster than the lignin; this initially rapid loss of easily soluble carbohydrate material would offset the slow rate of delignification, when both processes were considered together.

The decrease in the rate of delignification in the later stages of the process has been attributed to "burning" by Stangeland. In this series of experiments there was no visual evidence of "burning", but the cooking liquor became brownish in color. It is possible that the high concentration of products in the solution may retard the rate of reaction, or that the lignin remaining in the wood has undergone a change, owing to heating in acid solution. Such a change in lignin has been described in a previous paper (3).

The velocity constants listed in Table IV are obtained from the slopes of the more linear parts of the curves, and are not representative of the whole process. The reaction constant which Yorston (11) obtained by cooking spruce wood-meal was 0.67. This value is much greater than the value (0.35) obtained at 130° C. in this investigation, when chips were used, and also is greater than the value (0.49) obtained for wood-meal. Yorston calculated the constant from the steep linear portion of the curve, so that it represents a maximum value for those conditions. The average value would undoubtedly correspond much closer to the value reported here (0.49), which was calculated from the first order equation. Some variation would be expected, since the wood samples in the two cases did not come from the same tree.

It is interesting to consider the reaction mechanism that Stangeland (9) has suggested, in the light of these results. Stangeland quotes Hägglund, that when 16% (by weight) of the wood has gone into solution, the lignin should be fully sulphonated, *i.e.*, the sulphur expressed as percentage of the lignin should be about 8.6%. Stangeland concludes that this degree of sulphonation is reached in approximately two hours at 125° C., with a cooking liquor containing 3.03% free sulphur dioxide. Sulphonation is followed by a slow hydrolysis, which governs the actual rate of solution of the lignin as a whole. The rate of hydrolysis will depend on the temperature and the hydrogen ion concentration; the latter, Stangeland concludes, will remain fairly constant for any given liquor and cooking temperature, because of the buffer action of the lime.

The sulphur values listed in Table III show that, in this experiment, sulphonation continued throughout the whole course of the reaction, and a value of 8% was not reached until about 46% of the wood had gone into solution. This confirms the work of Yorston, showing that lignin continues to be sulphonated during the entire cooking process.

In 1929 Hägglund (7) reports cooking experiments carried out in buffer solutions on pulp that had previously been sulphonated, and shows that relatively small changes in the hydrogen ion concentration will produce quite appreciable changes in the rate of lignin removal. Although it is not definitely proved, it seems quite probable that the acidity of sulphite liquor increases during a cook, and Stangeland's assumptions of very rapid sulphonation and a constant pH appear hardly justified.

A tentative explanation is offered to account for the approximately first order rate observed in sulphite cooking. If the lignin is present in the wood

as submicroscopic particles or thin layers, the heating in aqueous solutions might tend to cause agglomeration. On the other hand, the cooking action would tend to decrease the particle size and accelerate the reaction rate. In the cooking process the two effects would be superimposed, and might cancel each other to give an approximately linear relation. If the colloidal nature of lignin is considered, this tendency to agglomerate does not seem entirely unlikely. Indeed Hägglund (8), in discussing the dissolving out of lignin by sulphonic acid, remarks that we are dealing not only with depolymerization, but also with the recombination of small particles to form larger particles. Whether the process is one of chemical polymerization, or purely physical agglomeration, is difficult to prove, but evidence of a change occurring in the lignin when wood is heated in aqueous solutions has been advanced in two previous papers (2, 3), and further evidence favoring an agglomeration process will be discussed in a future publication. The shape of the delignification curve would thus depend on the relative rates of the two processes discussed, and under some circumstances might deviate greatly from a straight line relation.

The residual lignin values reported in Table V were plotted to a logarithmic scale in Fig. 2, and straight lines were drawn as nearly through the points as possible. The values from Table III are also included for comparison.

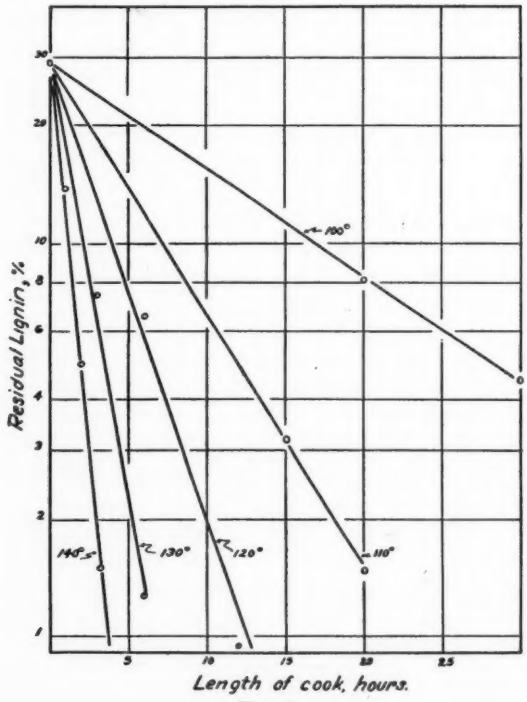

FIG. 2

These curves are intended merely to convey a picture of the change in the rate of reaction with a change in the temperature. In many reactions this change is expressed by the well known equation of Arrhenius,

$$ln\ k = ln\ z - \frac{E}{RT}.$$

Fig. 3, in which log k is plotted against the reciprocal of the absolute temperature, shows that the equation holds for the sulphite cooking reaction, since a linear relation is obtained. The energy of activation, E, is equal to the product of the slope of the line and R, the gas constant, expressed in calories (1.986). In this series of experiments it was found that,

$$E = 21{,}000 \text{ cal./gm. mol.}$$

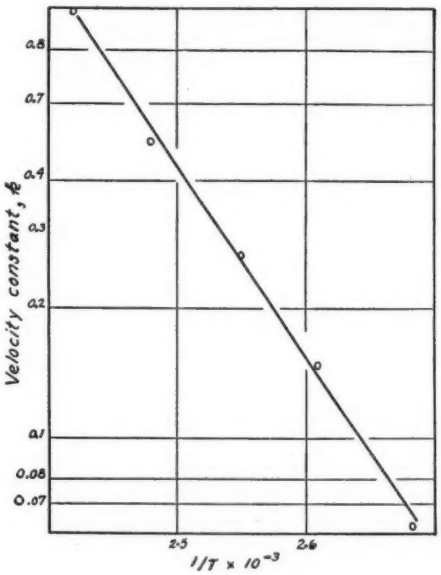

FIG. 3

The rate of reaction for the series reported in Table V was found, within experimental error, to double for a 10° C. rise in temperature.

Before concluding this discussion of the sulphite pulping process, a brief description of some experiments on the effect of pressure changes in cooking will be given.

The penetration apparatus was altered in such a way that the surface of the cooking liquor, during digestion, could be subjected to a known pressure of nitrogen gas. Thus at pressures below the vapor pressure of sulphur dioxide at the cooking temperature, a sulphur dioxide vapor phase could form, as happens in the commercial digester. With this apparatus the effect of pressure on the cooking process was examined over the range from five to ten atmospheres.

Black spruce chips, of density 0.36 and a chip length of 2 cm., were used and were cooked in calcium bisulphite liquor of composition: total SO_2, 5.10; free SO_2, 3.80; combined SO_2, 1.30%, for three hours at 140° C. The temperature was raised gradually to 140° C. in one hour; the total cooking period was therefore four hours.

It is evident from the data in Table VI, and from Fig. 4, that increase of the pressure beyond seven atmospheres has no effect on the rate of delignification or the quality of the pulp produced. The vapor pressure of the bisulphite solution used in this series was calculated from the data of Gishler (5), and found to be about seven atmospheres. Thus the slower

TABLE VI

EFFECT OF PRESSURE ON SULPHITE COOKING

Pressure, atm.	Yield of pulp, %	Yield of carbohydrate, %	Lignin in pulp, %	Residual lignin, %	Mullen strength, %
10	50.4	47.9	4.9	2.47	158
8	51.4	48.6	5.5	2.83	145
7	50.8	48.3	4.9	2.49	154
6	54.3	49.1	9.48	5.15	135
5	58.8	48.2	18.2	10.6	67

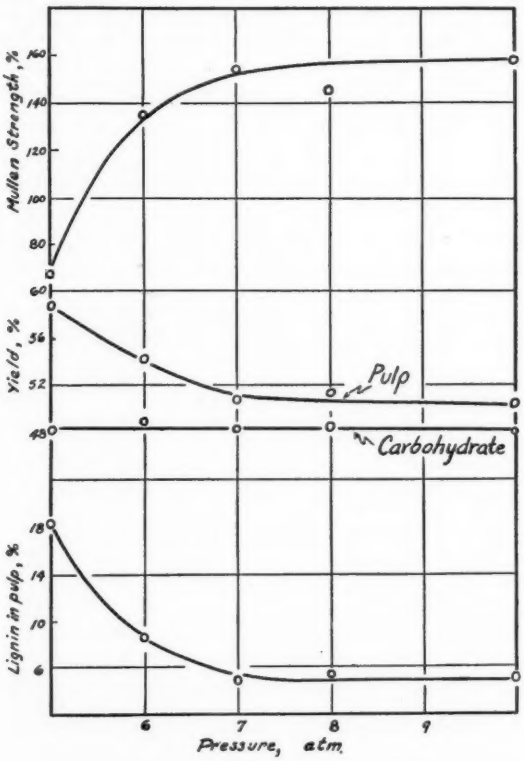

FIG. 4

cooking at pressures below seven atmospheres was due to the weakening of the cooking liquor through loss of sulphur dioxide, and not to a specific effect of the pressure. Although it has been shown that pressure during the cooking process is only a function of the temperature and liquor concentration, and has no specific effect on the reactions involved, it should be pointed out that pressure plays an important role in the beginning of the cook, by increasing the rate at which the cooking reagent penetrates the wood chips.

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